

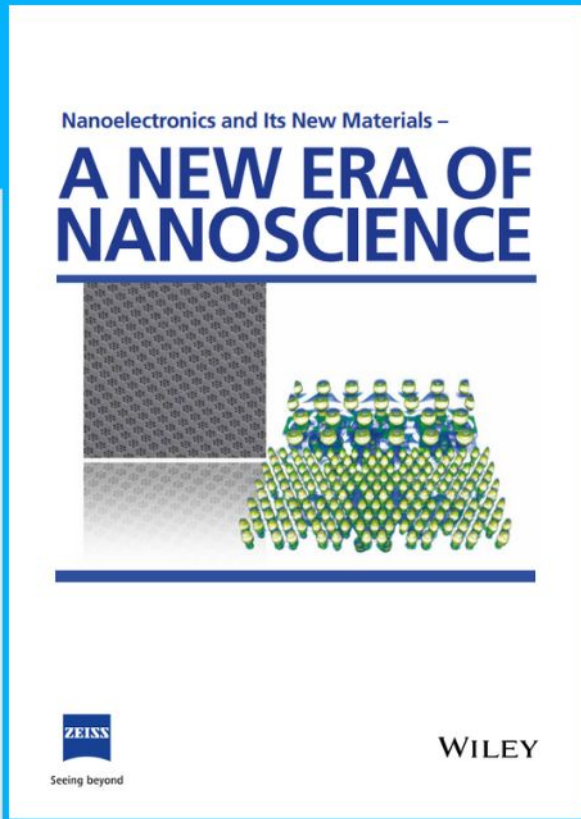


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# Precise Assembly of Highly Crystalline Colloidal Photonic Crystals inside the Polyester Yarns: A Spray Coating Synthesis for Breathable and Durable Fabrics with Saturated Structural Colors

Yuying He, Luyao Liu, Qianqian Fu,\* and Jianping Ge\*

It is a great challenge to prepare highly crystalline photonic crystal (PC)-modified fabrics with saturated colors without sacrificing the wearing experience, such as breathability and softness, at the same time. Here, a spray coating process is developed to precisely assemble the colloidal PCs inside every yarn of the polyester (PET) fabric. High surface tension and high boiling point for the solvent of colloidal solution, as well as low twist angle, large weave cycles, and large tightness for the fabric substrate, are found to be favorable to the formation of high-quality PC-modified fabrics. In addition, the as-prepared PC/PET fabrics have saturated and durable colors thanks to the highly crystalline PC structures and the polyacrylate adhesives. They also possess good softness and high breathability as the precise colloidal assembly in the yarn avoids the blocking of weaving holes and cracks.

in photonic crystals, there certainly will be no concern for environmental pollution. Therefore, the large-scale production of PC-modified fabrics with saturated color and good wearing experience has become a hot topic in the intersection of materials, optics, and textile industries.

One strategy for the fabrication of PC-modified fabrics is weaving by pre-made PC fibers. Here, the PC fibers can be prepared by the construction of PC structures on conventional fibers, including the confined colloidal assembly in the capillary tube,<sup>[3]</sup> dip coating<sup>[4]</sup> and electrophoretic deposition<sup>[5]</sup> of colloidal crystals, and wrapping with dielectric double layers.<sup>[6]</sup> Moreover, the PC fibers can also

## 1. Introduction


In the traditional textile industry, the dyeing of fabrics is usually achieved by the usage of chemical dyes, which absorb light with specific wavelengths and exhibit various colors. Although chemical dyes have been used by mankind for thousands of years, people still cannot fully address the color fading over time because the dyes will decompose or change in different environments. As the world steps into industrial civilization, a large amount of wastewater containing the residual dyes is produced, which leads to serious pollution for water and soil.<sup>[1]</sup> Recently, dyeing techniques based on the coating of photonic crystal (PC) were developed as a solution to the above challenges, as the structural colors are produced by the interference of light with the periodic structure<sup>[2]</sup> and are very stable in harsh environments for a long time. Since no chemical dyes are used

be directly prepared from the mixture of colloidal particles and polymer precursors using electrospinning<sup>[7]</sup> or microfluid spinning<sup>[8]</sup> processes. Although these methods are successful for the synthesis of PC fibers with tens to hundreds of micrometers in diameter, they were less efficient for the mass production of PC-modified fabrics, and the angular-dependent effect due to the curvature of fiber surface was also unfavorable to output uniform and bright colors in macroscale range.

Another strategy is preparing PC structures on various natural and chemical fabrics, which seemed to be a more feasible way to manufacture structural-color fabrics on a large scale with relatively low cost. Gravitational sedimentation<sup>[9]</sup> of colloidal PC on fabrics was the earliest attempt, which subsequently evolved into vertical deposition<sup>[10]</sup> and dip coating<sup>[11]</sup> of colloidal crystals. For example, Shao and Zhou et al.<sup>[9a]</sup> have prepared polyester (PET)-based PC-modified fabrics through the gradual sedimentation and self-assembly of melanin-like polystyrene@polydopamine particles on a fabric substrate. Later, the spray coating technique<sup>[12]</sup> was developed to realize rapid preparation of amorphous photonic crystal (APC)-modified fabrics, where the fast colloid assembly usually led to amorphous photonic structures with angular independent colors. For example, Zhang et al.<sup>[12a]</sup> have prepared APC silk fabrics with non-iridescence colors by one-step spray coating of poly(styrene-methyl methacrylate-acrylic acid) colloidal particles, polyacrylate (PA) adhesives, and carbon black. Recently, Yin et al.<sup>[13]</sup> optimized the blade coating process for the colloidal assembly of PS particles on PET fabrics, which produced a PC/PET fabric (1 m × 0.5 m) with uniform

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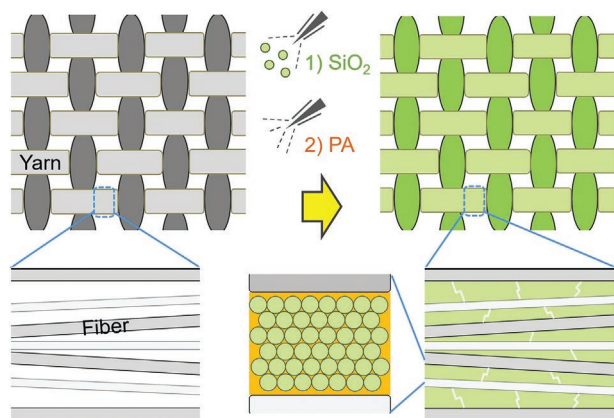
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and bright structural colors. In addition to the production of solid color fabrics, PC patterns on fabrics were also prepared by applicable methods, including inkjet printing,<sup>[14]</sup> screen printing,<sup>[15]</sup> and mask-assisted spraying,<sup>[12a,b]</sup> which further extended the synthetic methods for structural-colored fabrics.

All these synthetic approaches for PC-modified fabrics have revealed two common and urgent problems that require to be addressed. One is how to prepare highly crystalline PC structures with saturated colors on various fabrics with different chemical compositions, wettability, and microstructure. Different from the flat substrate commonly used in the assembly of colloidal PCs, the fabrics usually have porous, entangled structures, and uneven surfaces, which is unfavorable to the formation of long-range ordered structures. Another problem is how to retain the wearing experience of the source fabric after the deposition of PC structures. For the colloidal PC-modified fabrics, the loading of many rigid particles will inevitably decrease the softness and the breathability and change the touch feelings. Previous works usually paid more attention to the hue, brightness, and durability of structural colors, while the other wearable performances and their balance with the optical properties were hardly involved.

In this work, a spray coating method was developed to prepare breathable and durable PC/PET fabrics with saturated structural colors. Spray coating usually produced amorphous photonic crystal (APC) with unsaturated colors because the colloidal solution was atomized into tiny droplets under the shearing force and the accelerated solvent evaporation left a small window of time for colloidal assembly. Through the adjustment of physical properties of the colloidal solution and the microstructure of the fabric substrate, the spray coating was now able to produce highly crystalline PC structures on PET and PET blended fabrics on a large scale, which addressed the low saturation for structural-colored fabrics. Different from the previous methods, the spray coating provided a precise and restrained way to deposit colloidal crystals and adhesives only inside the PET yarns, which formed durable and breathable PC structures. Since the weaving holes and cracks were not blocked by the coatings, the as-prepared structural-colored fabrics showed higher breathability and good softness, which maintained the wearing experience of PET fabric to a great extent.



**Figure 1.** Scheme for the spray synthesis of  $\text{SiO}_2$ -PA/PET fabrics including Step 1) Spray coating of  $\text{SiO}_2$  colloidal particles on PET fabrics and Step 2) spray coating of PA adhesive nanoparticles followed by thermal treatment.

## 2. Results and Discussion

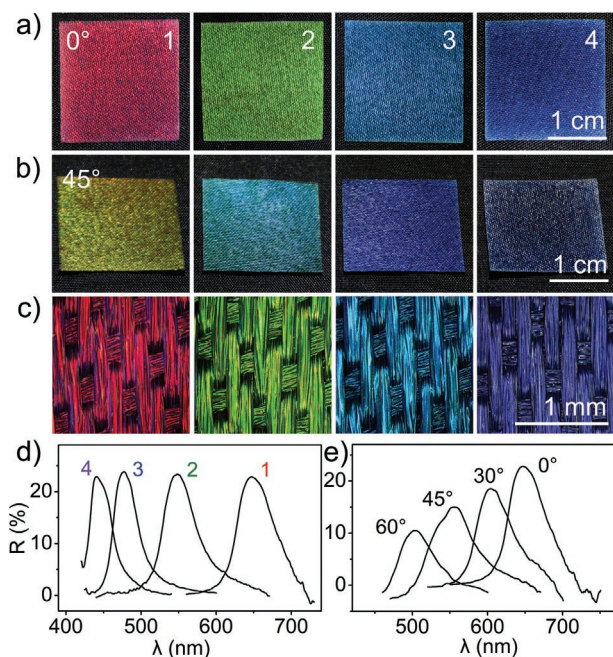
### 2.1. Precise Assembly of Colloidal PC on PET Fabrics via Spray Coating

As shown in **Figure 1**, a two-step spraying process was developed to prepare  $\text{SiO}_2$ -PA/PET fabrics with highly crystalline PC structure, saturated structural color, and soft, breathable, and durable characteristics. Generally, the PET fabrics were woven by warp and weft yarns in a specific weaving mode, where each yarn was composed of a bundle of fibers with a diameter of several tens micrometers. Therefore, the fabrics could be regarded as hierarchical porous structures with large cracks between the yarns and small gaps within the yarns. In the first spray of  $\text{SiO}_2$  colloidal solution, a thin liquid film quickly formed on the surface of PET fabrics, after which the colloidal solution with limited volume was fully absorbed into the porous yarns by capillary force. Along with the evaporation of the solvent in heating, the particles spontaneously precipitated to form a liquid colloidal PC and then transformed into a solid PC precisely located between the fibers and inside the yarns. In the following spray of PA adhesives, the PA nanoparticles were also enriched on the surface of the  $\text{SiO}_2$  particle-filled PET yarns due to the same capillary interactions. As the sample was heated above the glass transition temperature ( $T_g$ ) followed by being cooled down to room temperature, PA nanoparticles melted, solidified, and wrapped the PC structure and PET yarn to eventually produce a colorful and durable  $\text{SiO}_2$ -PA/PET fabric.

In the practical synthesis, the spray coating process was verified to produce PC/PET fabrics with uniform, saturated, and diverse structural colors. As shown in **Figure 2**, the PC-modified fabrics all possessed uniform structural colors because the spraying process fully atomized the colloidal solution and distributed them evenly to the fabrics. The porous structure of fabrics contributed to the uniform colors either, since the colloidal solution was immediately locked within a localized region after it was deposited onto the fabrics. The PC-modified fabrics also have highly saturated colors due to the high crystallinity of the  $\text{SiO}_2$  photonic structures. The color saturation of the red, green, blue, and purple fabrics was measured to be 25, 39, 37, and 41, which was higher than that of the amorphous PC-modified fabrics. (Table S1, Supporting Information) The high saturation could also be confirmed by the photos, the optical microscope (OM) images, and the angular dependency in color, which originated from the interference of incident light with the highly ordered periodic structures. As the incident and reflected angle changed from  $0^\circ$  to  $30^\circ$ ,  $45^\circ$ , and  $60^\circ$ , the reflection wavelength for the red PC-modified fabric changed accordingly from 650 to 605, 555, and 503 nm. It should be noted that the saturated colors could also be produced on white PET fabrics once a small amount of carbon black (0.3%) was added to the colloidal solution to absorb the incoherent scattering from the particles and substrate (Figure S1, Supporting Information). Similar to previous reports, the color of the fabrics could be tuned as red, green, blue, and purple to meet the requirement of different colors, where  $\text{SiO}_2$  particles with diameters of 277, 236, 199, and 189 nm were selected as the source materials.

Further characterization of the microstructures of the  $\text{SiO}_2$ /PET and  $\text{SiO}_2$ -PA/PET fabrics proved the precise colloidal assembly

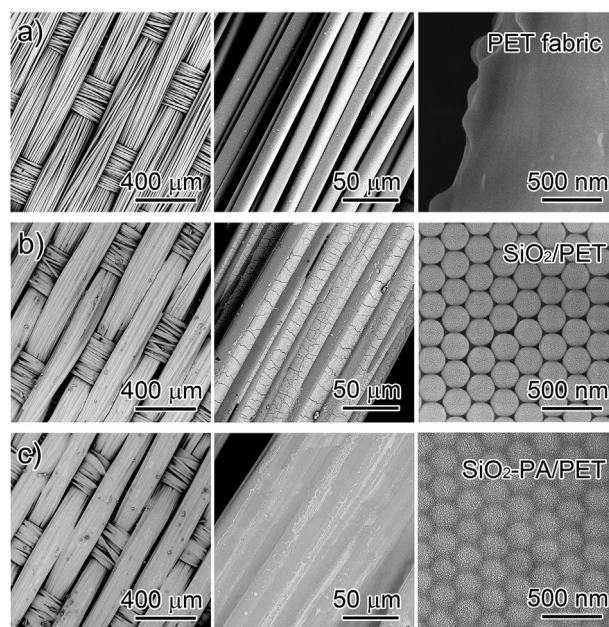




**Figure 2.** Highly crystalline  $\text{SiO}_2$ -PA/PET fabrics with angular-dependent colors. a,b) Digital photos under the viewing angles of  $0^\circ$  and  $45^\circ$ , c) optical microscope images, and d) reflection spectra of  $\text{SiO}_2$ -PA/PET fabrics prepared by  $\text{SiO}_2$  particles with diameters of (1) 277, (2) 236, (3) 199, and (4) 189 nm. e) Reflection spectrum of Sample 1 with the incident and reflected angles set as  $0^\circ$ ,  $30^\circ$ ,  $45^\circ$ , and  $60^\circ$ .

within the yarns, which was critical to the softness and breathability of the current material. The PET fabrics were woven with yarns, and each yarn was built from smaller fibers, which had a relatively smooth surface suitable for colloidal assembly (Figure 3a). In the first spraying process, the colloidal solution was absorbed into the yarns with small gaps by the capillary force so that the  $\text{SiO}_2$  particles assembled into PCs exactly within the yarns (Figure 3b). No colloidal assemblies were found to fill up the large cracks between yarns or cover the woven structure of the fabric no matter what kind of tightness the fabrics possessed (Figure S2, Supporting Information). It suggested that the deposition of PC structure by the current method was precise, restrained, and controllable. In order to achieve the precise assembly, the dosage and particle volume fraction of the colloidal solution for spray should be controlled below a critical value ( $75 \mu\text{L cm}^{-2}$ , 30%) to avoid excessive loading of colloidal materials and the formation of colloidal PC everywhere. (Figures S3 and S4, Supporting Information)

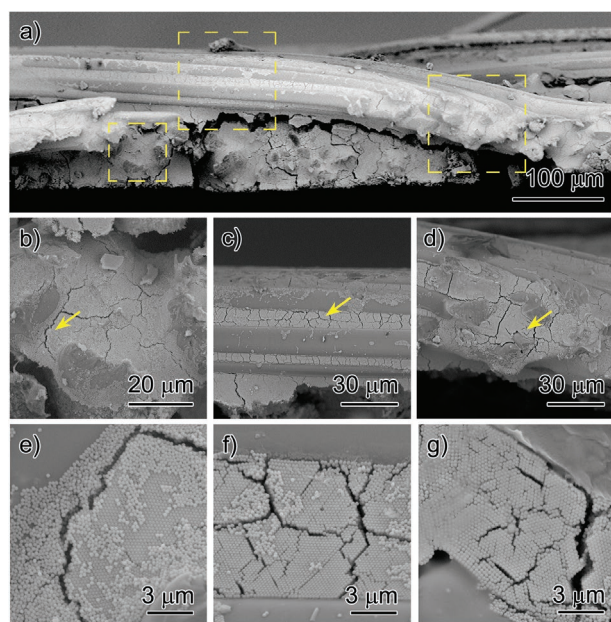
In the second spraying process, the PA adhesives were majorly deposited on the surface of the yarn or filled into the micron-scale cracks between the fibers or the colloidal crystals. Here, the PA adhesives were nanoparticles of poly(methyl methacrylate-co-butyl acrylate) with an average diameter of 90 nm prepared by emulsion polymerization (Figure S5, Supporting Information). During the spray coating of PA adhesives, its aqueous solution was also absorbed by the porous yarns due to the capillary interaction. However, since the PA nanoparticles were larger than the interparticle voids in colloidal crystals, they were blocked by the  $\text{SiO}_2$  particles between the fibers so that they could only deposit on the surface of the yarn. On the other



**Figure 3.** Precise deposition of  $\text{SiO}_2$  colloidal crystals and PA adhesives within the yarns. SEM images of a) the PET fabric, b) the typical green  $\text{SiO}_2$ /PET fabric, and c) the final  $\text{SiO}_2$ -PA/PET fabric.

hand, the PA nanoparticles might be brought into the micron-scale cracks between the fibers or the colloidal crystals along with the contraction of the solution during evaporation. Whatever, these two depositions were both favorable to the fixing of the colloidal crystals via thermal treatment. It should be noted that the PA adhesives were not deposited into the interparticle voids of colloidal PCs since the reflection peak of PC before and after spray coating of PA had the same wavelength (Figure S6, Supporting Information). Finally, the spray coating of PA and the thermal curing would not affect the ordered PC structure at all, as proved by the scanning electron microscope (SEM) image of  $\text{SiO}_2$ -PA/PET fabric (Figure 3c). The  $\text{SiO}_2$  colloidal PCs were firmly stabilized on the PET fabrics by the PA adhesives, which formed almost independent PC yarns with good mechanical stability.

Since the  $\text{SiO}_2$  particles were precisely assembled inside the yarns and fixed by the PA adhesives, the as-prepared  $\text{SiO}_2$ -PA/PET fabric could even be disassembled into separated PC-modified yarns under the premise of not destroying the photonic structures (Figure S7, Supporting Information). When a Satin fabric was disassembled into weft and warp yarns, they were easy to be separated from each other, which proved that there were no colloidal PCs or PA adhesives between the yarns. The single weft yarn still showed the structural color in the OM due to the complete reservation of PC structures. In the top-view SEM image, the intersecting nodes of the weft and warp yarns were periodically observed on the single yarn, where the particles were usually arranged in disordered states. However, in the yarns between two nodes that were exposed to the observers, the particles assembled into ordered structure between fibers and fixed by the PA adhesive to form a complete PC-modified yarn. Although the colloidal particles were embedded by the PA adhesives, their ordered assemblies could be vaguely discovered



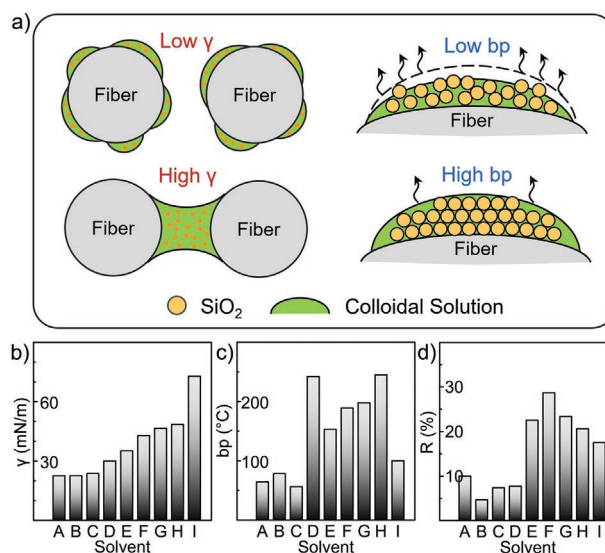
**Figure 4.** Cross-sectional SEM images of the yarn. SEM images of a) the SiO<sub>2</sub>-PA/PET fabric, which was zoomed in to show the cross-sectional view of b), e) the warp and d), g) weft yarn, and the side view of c), f) the weft yarn.

in some places. In the cross-sectional and side-view SEM image (Figure 4), it was also very clear to find the ordered colloidal assemblies between the fibers within the yarn. All these in situ observations firmly demonstrate the precise colloidal assembly in the current synthesis.

## 2.2. Tuning the Colloidal Assembly in Spray Synthesis

The recipe of colloidal solution, especially the selection of solvent, was found to be critical to the colloidal assembly in the spraying synthesis of SiO<sub>2</sub>-PA/PET fabrics. Here, SiO<sub>2</sub> particles were dispersed in nine kinds of regular solvents to form homogeneous solutions with the same particle volume fraction of 20%, which were sprayed onto the same substrate to prepare PC-modified fabrics for comparison. The structural-colored fabrics prepared by the colloidal solution from *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), diethylene glycol (DEG), ethylene glycol (EG), and water showed clear structural colors, and their OM and SEM images also confirmed that the SiO<sub>2</sub> particles were assembled into ordered colloidal crystals between the fibers and within the yarn (Figures S8 and S9, Supporting Information). However, the fabrics prepared by the colloidal solution from methanol (MeOH), ethanol (EtOH), acetone (ACE), and propylene carbonate (PCb) scarcely possess structural colors because the SiO<sub>2</sub> particles agglomerated into amorphous stackings and were randomly distributed on the surface of PET fibers. It seemed that the SiO<sub>2</sub> particles were not concentrated effectively with the contraction of solution during evaporation in these cases, and particles also had no adequate time for assembly before the sample was fully dried.

The experimental results urged us to explore the intrinsic physical property of the solvent that dominated the colloidal

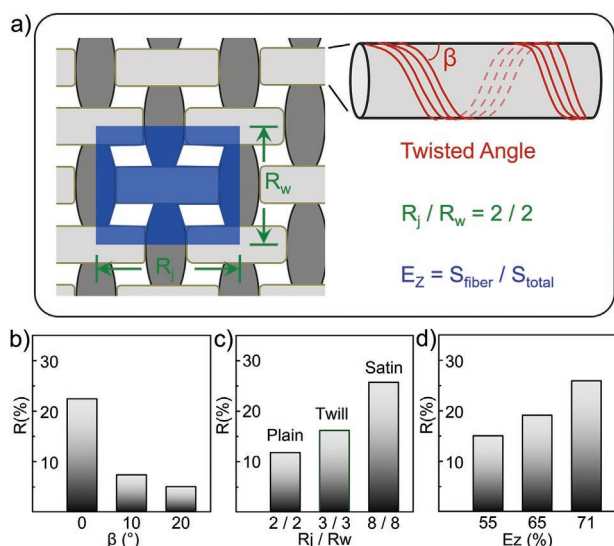


**Figure 5.** Influence of solvent upon colloidal assembly. a) Influence of dispersion solvent upon colloidal assembly. b) Surface tensions and c) boiling points of the solvents, including (A–I) MeOH, EtOH, ACE, PCb, DMF, DMSO, EG, DEG, and H<sub>2</sub>O. d) Reflection intensity of the PC-modified fabrics prepared by colloidal solutions with these solvents.

assembly. When the solvents were arranged in the sequence of increasing surface tension ( $\gamma$ ) and boiling point (bp), one could find that they matched the reflection intensity, which indicated the assembly quality quite well (Figure 5). A high surface tension ensured the movement of SiO<sub>2</sub> particles with the contraction of solution and the effective concentration in the gaps between the fibers, which led to precise assembly inside the yarn but not on its surface. On the other side, a high boiling point left sufficient time for colloidal assembly, which formed highly crystalline PCs instead of disordered stacking. In a word, solvents with high surface tension and boiling point were more suitable for the spray coating. It should be noted that such a conclusion provided rough criteria for the selection of solvent. It was not meant to be applied to any specific two solvents as a precise law because the colloidal assembly was a complicated process that could be affected by many other parameters. For example, DEG led to a relatively lower reflectance than DMF/DMSO, maybe because its much higher viscosity blocked the colloidal assembly during solvent evaporation.

The colloidal solutions from the PCb and water were special as they had inconsistent surface tension and boiling point. The PCb solution with low  $\gamma$  and high bp eventually failed to produce structural-colored fabric, while the aqueous solution with large  $\gamma$  and relatively low bp had achieved success. It was interesting that the PCb solution of colloidal particles was usually a better precursor than the aqueous solution for most synthesis of PC films on flat surfaces, such as glass and PET film. However, the assembly results were just the opposite here, which suggested that enrichment of particles into the yarns due to the high surface tension was probably a precondition for preparing the highly crystalline PC structure on a fabric substrate. These understandings provided more clear standards to select solvent for colloidal solution precursors, which enabled us to prepare highly crystalline PC structures on fabrics.





**Figure 6.** Influence of microstructures of fabrics upon colloidal assembly. a) Microstructure of fabrics described by the twisted angle ( $\beta$ ), the weaving mode ( $R_j/R_w$ ), and the tightness ( $E_z$ ), and b–d) their influences upon colloidal assembly and reflection intensity.

Besides the solvent and colloidal solution, the microstructures of the fabric substrate were also critical to the colloidal assembly, which was scarcely studied in the previous works. As shown in **Figure 6**, the PET fabrics were woven by yarns with specific weaving mode and tightness, while each yarn was composed of a bundle of fibers with a certain twist angle to improve its mechanical strength. These parameters determined the fabric's structure and thereby significantly affected the colloidal assembly on them. For example, the yarn with a twisted angle ( $\beta$ ) of  $0^\circ$  was composed of parallel fibers, and most of the colloidal crystals formed between the fibers had the same orientation so that they reflect the same structural color with strong intensities. However, as  $\beta$  increased to  $20^\circ$ , the yarn was now composed of parallel but helical fibers. Although the colloidal crystals also formed between the fibers, their orientation continuously changed with the distortion, and the reflection intensity decreased as the crystal orientation was tilted away from the incident light, which explained why only a thin bright green line was observed on the  $\text{SiO}_2$ -PA/PET yarn with  $\beta$  of  $20^\circ$ . Therefore, the overall reflection intensity decreased, and the structural color faded accordingly (Figures S10 and S11a–c, Supporting Information). Similarly, as the weaving mode was switched from the Satin, Twill, to Plain mode, that is, the ratio of warp/weft weave cycles ( $R_j/R_w$ ) decreased from 8/8, 3/3, to 2/2, a large amount of continuous space for the colloidal assembly was split into smaller spaces by the nodes of warp and weft yarns, which lead to the fading of structural colors, either (Figure S11d–f, Supporting Information). Furthermore, as the tightness of the fabric ( $E_z$ ) increased from 55% to 71%, the reflection intensity and the observed color were enhanced because there would be more places for assembly in the unit area as the fabric was woven in a tighter way (Figure S11g–i and Table S2, Supporting Information).

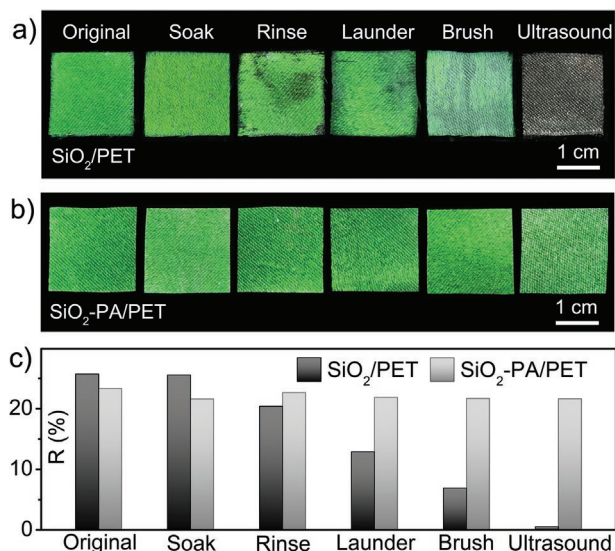
The above study on the microstructure of fabric suggested that the spraying process was suitable for the synthesis of PC

coatings on fabrics made from flat, straight, and untwisted fibers. Based on the preliminary experiments, it was difficult to prepare highly crystalline PC structures on cotton and wool fabrics, as their yarns twisted too much to achieve large colloidal crystals. Fortunately, the current spray coating could be extended to most PET-contained blended fabrics, such as the “polyester-cotton” and the “polyester-spandex” fabrics (Figure S12, Supporting Information), probably there was still part of the pores and gaps suitable for colloidal assembly.

### 2.3. Wearing Performance of $\text{SiO}_2$ -PA/PET Fabrics

The mechanical stabilities, including the resistance to friction, soaking, and washing, were fundamental requirements for fabrics dyed with structural colors. Here, we have designed five kinds of durability tests, including soaking in water for 2 h, rinsing by water for 10 min, laundry for 45 min, being brushed 50 times, and sonication for 10 min for both the  $\text{SiO}_2$ /PET and  $\text{SiO}_2$ -PA/PET fabrics. The color fastness in the laundry was evaluated according to the American Association of Textile Chemists and Colorists standard 61–2013 (AATCC TM61-2013), which was tested in water at  $40^\circ\text{C}$  with a volume fraction of liquid detergent set as 0.3%. Typical Photos and average reflection intensity from three parallel tests were used to evaluate their mechanical stabilities (**Figure 7**). The experimental results suggested that a mild soaking operation had little influence upon both two fabrics, and the structural colors were retained quite well after the samples were dried. When the fabrics were rinsed by water or washed by a laundry machine, the  $\text{SiO}_2$ /PET fabric lost color in part of the region because there is no strong interaction between the  $\text{SiO}_2$  PC and PET, so the PC structure easily peeled off from the supports under external forces. However, the  $\text{SiO}_2$ -PA/PET fabric remained unchanged in color because the PA adhesives could firmly adhere the  $\text{SiO}_2$  PCs to the PET fabrics through heating above its glass transition temperature and cooling down to room temperature. When more violent operations, such as brushing and sonication, were applied to the PC-modified fabrics, the PC structures on  $\text{SiO}_2$ /PET were severely damaged, but those on  $\text{SiO}_2$ -PA/PET were still well retained. Since the above experiments could simulate most of the cleaning methods, including hand-washing and machine washing, the as-prepared  $\text{SiO}_2$ -PA/PET fabrics were proved to be durable and practically usable in daily life. Because the introduction of PA adhesives had a negligible influence on the structural color, the spray of an aqueous solution of PA nanoparticles followed by heat treatment could be a good solution to improve the stability of colloidal PC-modified fabrics.

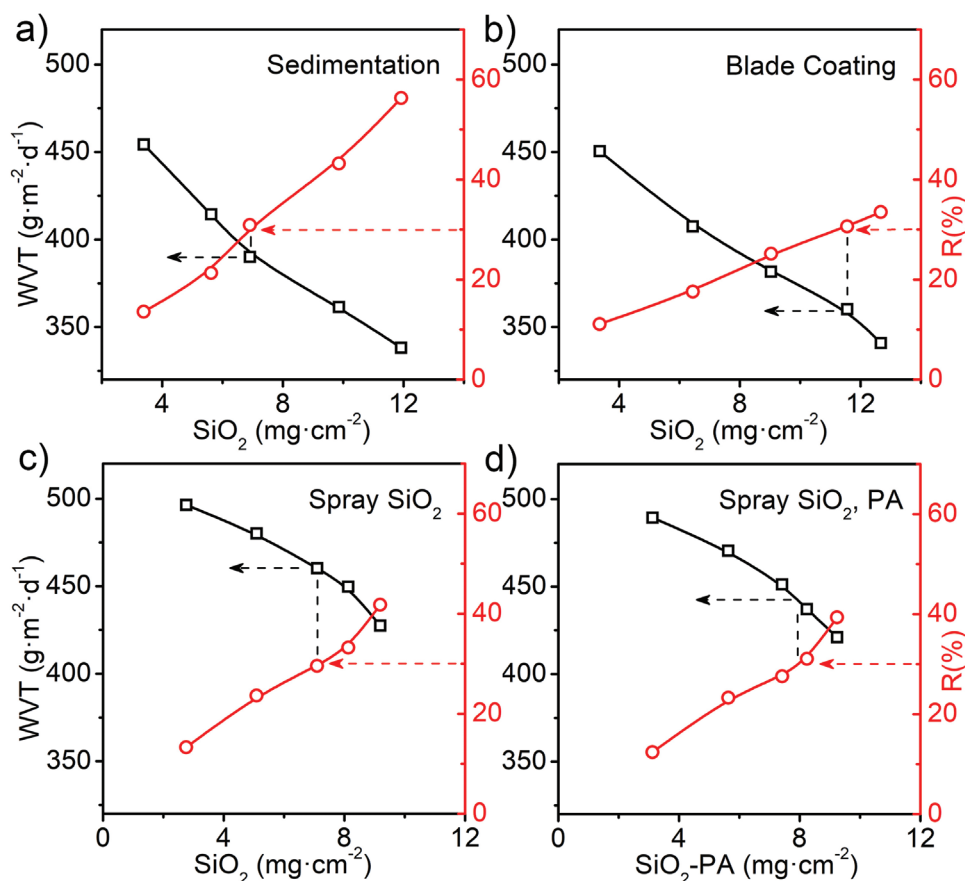
Breathability was another important standard to evaluate the comforts of PC-modified fabrics, especially when a large amount of small colloidal particles and adhesives were deposited on the porous fabrics. Previous works usually paid more attention to the hue and brightness of structural colors and their durabilities, but the evaluation of breathability was never included. Here, we had prepared four kinds of PC/PET fabrics by gravitational sedimentation, blade coating, and spray coating. The permeability indicated by the water-vapor transport (WVT) values, the  $\text{SiO}_2$  particle loading per unit area, and the color brightness indicated by the reflection intensity were



**Figure 7.** The durability of the PC/PET fabrics. a,b) Photos and c) reflection intensity of SiO<sub>2</sub>/PET and SiO<sub>2</sub>-PA/PET fabrics after durability tests, including soaking in water for 2 h, rinsing by water for 10 min, laundry for 45 min, being brushed 50 times, and sonication for 10 min.

measured (Tables S3–S6, Supporting Information) and plotted in one figure to compare the performance of fabrics from different synthetic methods (Figure 8). All the fabrics showed some same characteristics that the color brightness enhanced with the increasing of particle loading, and its permeability decreased accordingly. However, the permeabilities corresponding to the same color brightness were different for these fabrics. For instance, when the reflection intensity was required to reach 30%, the particle loadings for SiO<sub>2</sub>/PET prepared by sedimentation and blading coating and the loadings for SiO<sub>2</sub>/PET and SiO<sub>2</sub>-PA/PET from spray coating were measured to be 6.9, 11.5, 7.2, and 7.9 mg cm<sup>-2</sup>, and the corresponding WVT were measured to be 390, 359, 460, and 442 g m<sup>-2</sup> day<sup>-1</sup>. Apparently, the permeability of the PC-modified fabrics prepared by spray coating was closer to that of the original PET fabric with a WVT of 552 g m<sup>-2</sup> day<sup>-1</sup>.

The hand perceptions of the original and PC-modified fabrics were evaluated by a bipolar comfort attribute method according to the standard AATCC Evaluation procedure 5–2007. The evaluators were requested to touch the fabric in the way of folding, stroke, pinching, pulling, and rubbing (Figure S13, Supporting Information), and evaluate the fabrics subjectively with a score from 1 to 5, which quantified the hand perceptions



**Figure 8.** The breathability of the PC/PET fabrics. The WVT values, the particle loadings, and the reflection intensity of the SiO<sub>2</sub>/PET fabrics prepared by a) sedimentation and b) blade coating, and those of c) SiO<sub>2</sub>/PET and d) SiO<sub>2</sub>-PA/PET fabrics prepared by spray coating.

in the aspects of roughness, softness, heavy feeling, dryness, and comfortable feeling (Table S7, Supporting Information). The average results from ten evaluators suggested that although the SiO<sub>2</sub>-PA/PET fabric became a little rough, stiff, and heavier than the original PET fabric, its hand perceptions were basically retained after modification of PC structures.

The superior breathability and softness of the structural-colored fabrics prepared by spray coating originated from the precise assembly of highly crystalline PC structures inside the PET yarns. On the one hand, an accurate colloidal assembly inside the yarn could avoid not only the deposition of particles in the weaving holes but also the formation of the densely continuous film after the introduction of PA adhesives, which effectively improves the breathability and softness of colloidal PC-modified fabrics. It might be difficult to realize such precise assembly by sedimentation and blade coating. On the other hand, the current spray synthesis possessed the highest utilization of colloidal materials where the particles were assembled into crystalline PC structures as much as possible. The crystalline structure not only decreased the incoherent scattering and enhanced the color brightness but also decreased the loading of particles and thereby retained the wearing experience of original fabrics.

The as-prepared SiO<sub>2</sub>-PA/PET fabrics exhibited many superior properties, including saturated structural color, durable and firm dyeing, soft and breathable texture, easiness in patterning, and large-scale production (Figure 9). Benefitting from the high crystallinity of PC structure, the structural-colored fabrics showed saturated colors without any feeling of pale white appearance from the incoherent scattering of SiO<sub>2</sub> particles. The angular dependency in color was another proof to support

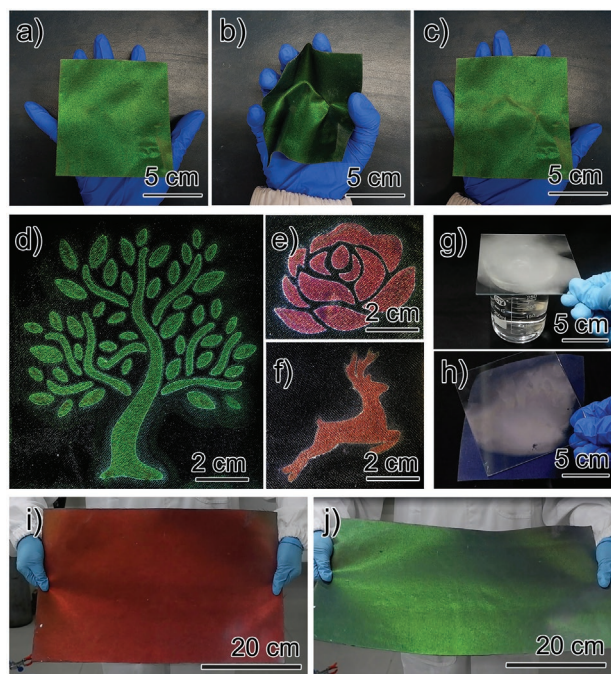
the high crystallinity. The precise colloidal assembly inside the yarns ensured the soft and breathable texture. The fabrics showed little changes in color after repeated rubbing and folding. When the fabric was placed between the hot water and a dry glass slide, water fog could be observed on the glass immediately, which confirmed its good breathability (Video S1, Supporting Information). Furthermore, the spray coating had inherent advantages in patterning and large-scale production (Video S2, Supporting Information). With the assistance of hollow marks, PC patterns of trees, flowers, and deer could be easily prepared on PET fabrics. When the colloidal solution was sprayed to the fabrics, the porous structure and the strong capillary interaction made it easy to spread the colloidal solution on the surface of the fabric to form very uniform PC coatings in the end.

The current spray technology might be extended to the fabrication of stimuli-responsive fabrics based on the integration of responsive materials.<sup>[16]</sup> The best way was the one-step spraying of the colloidal solution containing both the particles and the responsive prepolymers. However, the choice of the responsive material might be very limited as it must meet the requirements of colloidal assembly and structural fixing simultaneously. A more feasible way was replacing the PA adhesives in the second spray coating with responsive prepolymers, which could introduce a responsive matrix with more functions without worrying about destroying the high crystallinity of PCs.

### 3. Conclusions

In summary, a two-step spray coating method had been developed to prepare photonic crystal-based PET and its blended fabrics with saturated structural colors, durable dyeing, as well as soft and breathable textures. Systematic studies on synthesis suggested that high surface tension and high boiling point for the solvent of colloidal solution, as well as low twist angle, large weave cycles, and large tightness for the fabric substrate, were all favorable to the formation of highly crystalline and high-density PC structures on PET fabrics. Different from the previous methods, the current spray coating provided a precise, restrained, and controllable way to deposit PC structures and adhesives only in the yarns based on the capillary interactions from the fabrics and the tuning of physical parameters of colloidal solution. The colloidal particles were only assembled between the fibers inside every yarn, and the following deposition of PA adhesives only enriched around the yarn either, which eventually formed independent and fixed PC composite yarns.

It was worth being noted that the colloidal assembly inside the yarn avoided the blocking of weaving holes and the formation of a dense and continuous coating, which effectively improved the breathability of the PC-modified fabrics. Highly crystalline PC structures enhanced the color brightness and decreased the dosage of the particle to the minimum, which improved the softness and comfort of the fabrics. The introduction of PA adhesives could improve the durability of the PC-modified fabric without sacrificing its color and wearing comfort. Based on the above merits of the spray coating and its inherent advantages in patterning and large-scale production, it could be developed as a potentially useful method to prepare various structural color fabrics with better qualities.



**Figure 9.** Exhibition of the PC/PET fabrics. Digital photos of the SiO<sub>2</sub>-PA/PET fabrics showing the a–c) soft, d–f) patternable, g,h) breathable, i,j) angular-dependent characteristics and its potential for large-scale synthesis.



## 4. Experimental Section

**Materials:** Tetraethyl orthosilicate (TEOS, 98%), aqueous ammonia ( $\text{NH}_3 \cdot \text{H}_2\text{O}$ , 28%), potassium persulfate (KPS, 99.5%), DMF (99.5%), DMSO (99%), and MeOH (99.5%) were obtained from Sinopharm Chemical Reagent Co. Ltd. Arginine (98%), PCB (99%), butyl acrylate (BA, 99%), and sodium dodecylbenzene sulfonate (SDBS, 95%) were obtained from Aladdin Co. Ltd. EG (99%) and DEG (99%) were purchased from J&K Co. Ltd. ACE (99.5%) was purchased from Jiangsu QiangSheng Functional Chemical Co. Ltd. Methyl methacrylate (MMA, 99.8%) was purchased from Tokyo Chemical Industry Co. Ltd. Carbon black (Emperor 1800) was obtained from Carbot Co. Ltd. All chemicals were used as received without further purification. All the PET and blended PET fabrics with different twisted angles, weave modes, and tightness were commercial products purchased from the local dealers.

**Synthesis of  $\text{SiO}_2$  Colloidal Particles:** The monodisperse  $\text{SiO}_2$  nanospheres were synthesized by a two-step seeding growth process. In a typical synthesis of  $\text{SiO}_2$  particles with an average diameter of 236 nm, TEOS (5.55 mL) and arginine (0.087 g) were dissolved in water (87 mL) in a three-necked round-bottom flask under magnetic stirring, which was heated at 70 °C for 24 h to obtain a  $\text{SiO}_2$  seed solution. Then, a small amount of seed solution (400  $\mu\text{L}$ ) was added to the mixture of water (70 mL), EtOH (1 L), and  $\text{NH}_3 \cdot \text{H}_2\text{O}$  (40 mL), after which TEOS (80 mL) was gradually injected with a speed of 10 mL  $\text{min}^{-1}$  to produce the  $\text{SiO}_2$  particles in 12-h reaction. Finally, the  $\text{SiO}_2$  colloidal particles were washed three times with EtOH and stored in EtOH for later usage.  $\text{SiO}_2$  particles with diameters of 277, 199, and 189 nm could be prepared by similar methods, except that the volume of  $\text{SiO}_2$  seed solution was adjusted to 250, 600, and 800  $\mu\text{L}$ .

**Synthesis of PA Nanoparticle Adhesives:** The poly(methyl methacrylate-co-butyl acrylate) (PA) copolymer nanoparticles were prepared by emulsion polymerization. Typically, MMA (5 g), BA (5 g), and SDS (0.6 g) were dissolved in water (90 mL) to form a homogeneous solution in a four-necked flask. After heating the mixture to 80 °C, an aqueous solution of KPS (10 mL, 3wt%) was added to the reactor to initiate the polymerization. PA nanoparticles emulsion was obtained after 5 h of reaction under mechanical stirring, which was used directly for spraying without further purification.

**Preparation of  $\text{SiO}_2$ -PA/PET Photonic Crystal Fabrics via Spray Coating:** Generally,  $\text{SiO}_2$  colloidal particles were dispersed in different solvents, such as EG, DMF, and water, to form colloidal solutions with a volume fraction of 20%. In the first spraying, the colloidal solution (100  $\mu\text{L}$ ) was sprayed onto the PET fabric with an area of  $2 \times 2 \text{ cm}^2$ . The spray gun (U-STAR S-120) with a nozzle diameter of 0.2 mm was placed 5 cm away from the fabric, and the spray coating was driven by compressed air with a pressure of 0.103 MPa. The sample was dried in an oven at 90 °C for 5 min to obtain  $\text{SiO}_2$ /PET fabric. In the second spraying, the emulsion of PA nanoparticle (100  $\mu\text{L}$ ) with a weight percentage of 6.6% was sprayed onto the  $\text{SiO}_2$ /PET fabric under the same conditions, after which the sample was thermally cured at 90 °C for 1 min to form the  $\text{SiO}_2$ -PA/PET photonic crystal fabrics eventually.

**Preparation of  $\text{SiO}_2$ /PET Photonic Crystal Fabric via Blade Coating:** Monodisperse  $\text{SiO}_2$  particles were first dispersed in EG to form a colloidal solution with a volume fraction of 40%. The colloidal solution was linearly spread on one edge of the PET fabric and then blade coated onto the whole fabric by the OSP extrusion wire bar coaters. Eventually, the  $\text{SiO}_2$ /PET photonic crystal fabric was prepared after evaporation of solvent at room temperature with a humidity of 60%.

**Preparation of  $\text{SiO}_2$ /PET Photonic Crystal Fabric via Gravitational Sedimentation:** Monodisperse  $\text{SiO}_2$  particles were dispersed in EG to form a colloidal solution with a mass fraction of 1.5%. A piece of PET fabric substrate was immersed into the above  $\text{SiO}_2$ /EG solution in a petri dish, which was transferred to an oven at 90 °C for 12 h to evaporate the solvent and produce the  $\text{SiO}_2$ /PET photonic crystal fabric.

**Characterizations:** The photos of photonic crystal fabrics were captured by a Fujifilm X-A5 digital camera. The OM images were collected by an Olympus BXFM reflection-type microscope operated in dark-field mode. The colloidal assembly of  $\text{SiO}_2$  photonic crystals was

characterized by a Hitachi S4800 SEM. The microstructure of the fabrics was characterized by Phenom G2 Pro SEM. The reflection spectra of the PC-modified fabrics were measured by an Ocean Optics Maya 2000 Pro spectrometer coupled with a six around one reflection probe. The incident and reflective angles were fixed at 0° except for the angular-dependent experiments. The reflection intensities ( $R$ ) in Figures 5–8 were the average value of the intensities measured at five random positions on the fabrics.

**Measurement of Water-Vapor Transport Values of PC-Modified Fabrics:** The WVT values describing the moisture permeability of the fabrics were measured by the following procedures. First of all, a glass beaker filled with 80% of distilled water in volume was covered and sealed by the tested PC-modified fabrics. The beaker was transferred to a stable environment with a temperature of 25 °C and humidity of 60% for 2 days, during which part of the water evaporated and diffused to the air through the fabrics. Finally, the WVT values in the unit of  $\text{g m}^{-2} \text{d}^{-1}$  could be calculated by the following equation, where  $\Delta m$  was the mass loss of the distilled water,  $S$  was the coverage area of the fabrics, and  $t$  was the evaporation time in the unit of the day. The WVT values listed in this work were the average values from three parallel measurements.

$$\text{WVT} = \frac{\Delta m}{S \times t} \quad (1)$$

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

## Keywords

breathable, durable, highly crystalline, photonic crystal fabrics, precise assembly

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